

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

M.A./M.SC. SECOND SEMESTER EXAMINATION, MAY 2012

FIRST YEAR

APPLIED CHEMISTRY

Date : 25/05/2012

Time : 11 am – 1 pm

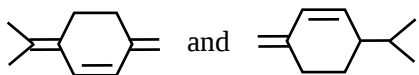
Paper : VII

Full Marks : 50

[Use separate Answer Books for each Group]

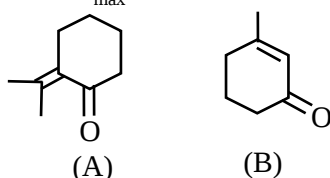
Group - A

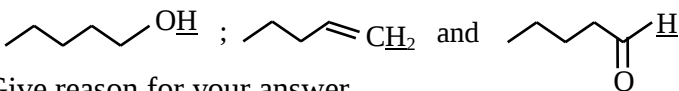
(Answer any one question)

1. a) Which one of the following two polyenes will have higher $\lambda_{\max}$ value for uv absorption? Justify your answer. [2]
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- b) Explain bathochromic shift and hyperchromic effect with example. [2]
- c) Between cis- and trans-1, 2-dichloro ethene, which one is I.R. inactive and why? [2]
- d) Arrange with justification the γ_{C-H} stretching frequencies of ethane, ethene and ethyne in order of decreasing value. [2]
- e) Suggest a structure of a compound which shows ion peaks at m/z values 156, 158 (intensity 1 : 1), 159, 77(base peak), 51. Given the ratio of peak m/z 159 : m/z 158 = 6·2 : 92·5. Explain the mass fragmentations observed. [4]
- f) What do you understand by 'upfield proton' in NMR spectroscopy? [1]
- g) A compound of molecular formula $C_{11}H_{16}$ shows three signals with integration ratio a : b : c = 8·8 : 2·9 : 3·8. How many protons give rise to each signal? [2]
2. a) Designate the following uv absorption bands for acetophenone with reasons : [2]
319 (ϵ 50); 240 (ϵ 13000); 278 (ϵ 1110).

Or,

Calculate the $\lambda_{\max}$ values for A and B.

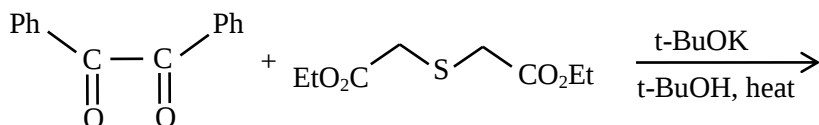


- b) The two geometrical isomers of stilbene show $\lambda_{\max}$ at 294 and 278 nm. From this piece of information designate their structures with explanation. [2]
- c) Match the following $\gamma_{C=O}$ stretching frequencies with appropriate derivative of $\begin{matrix} R & & Z \\ & \diagdown & / \\ & C & \\ & // & \\ & O & \end{matrix}$, where $Z = NH_2, Cl, OEt$ [2]
[$\gamma_{C=O}$] given $1815cm^{-1}, 1750cm^{-1}, 1690cm^{-1}$. Give reasons for your answer. [3]
- d) What do you understand by McLafferty cleavage in mass spectrometry? Explain with a suitable example. [2]
- e) How can you identify a metastable ion peak in mass spectrum? Which (m/z) would you expect a meta stable ion if the parent ion (m/z) = 91 breaks into a daughter ion (m/z) = 65? [2]
- f) Arrange, in decreasing order, the chemical shifts (δ values) of the labeled protons of  [3]
Give reason for your answer. [3]
- g) How many signals would you observe in the 1H -NMR spectrum for vinyl chloride? [1]

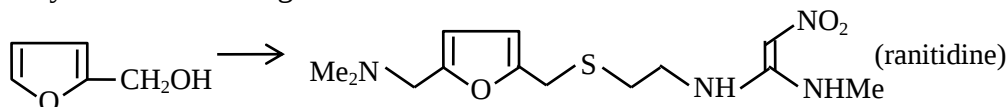
Group - B

(Answer **any one** question)

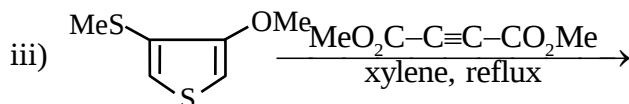
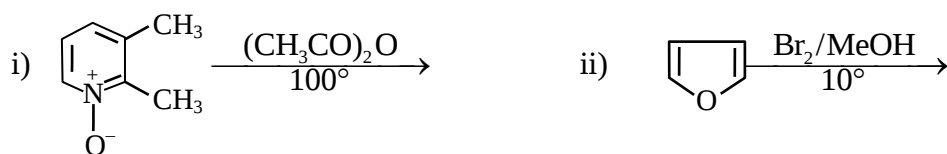
3. a) Write the structure of the thiophene derivative which would be produced in the following reaction. Give mechanism of the reaction. [2½]



- b) Carry out the following transformation : [2½]



- c) Write the product(s) of the following reactions with suitable mechanism in each case (**any two**) : [1½×2]

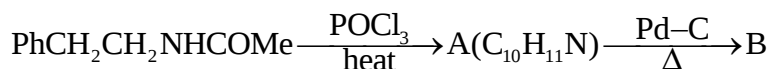


- d) Answer **any two** : [2×2]

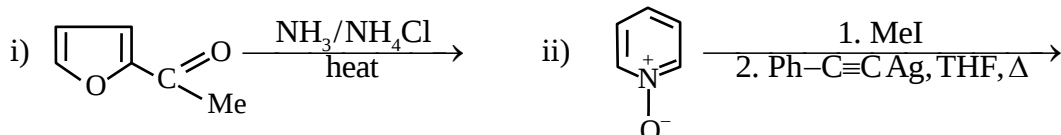
- Oxidation of D-fructose with Tollen's reagent yields a mixture of D-mannonic acid and D-gluconic acid. Account for the observation.
- When D-glucose is refluxed with methanol in the presence of HCl, both anomers of methyl-D-glucopyranoside are formed. Give the mechanism of their formation in chair perspective formula.
- Convert : D-glucose $\longrightarrow$ 3-deoxy-D-glucose.

- e) Outline a synthesis of (±)-nicotine highlighting the key steps involved therein. [3]

4. a) Write the structures of A and B in the following reactions and give mechanism of formation of A. [2½]



- Indole undergoes electrophilic substitution primarily at C – 3 but pyrrole does at C – 2. Explain. [2]
- Pyrrole on reaction with chloroform and a strong base gives 3-chloropyridine as one of the products. —Explain its formation. [1½]
- Predict the product(s) in the following reactions with plausible mechanism. (**any one**) : [2]



- e) Answer **any two** : [2×2]

- Write the structures of D-glucose and another aldohexose which on oxidation with nitric acid yield the same aldaric acid. Would they form same osazone? Explain.
- Convert : D-arabinose $\longrightarrow$ D-fructose

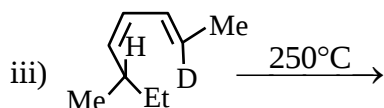
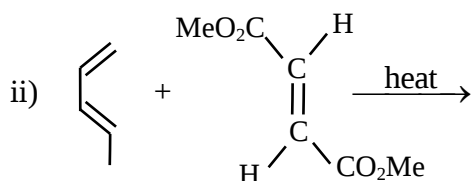
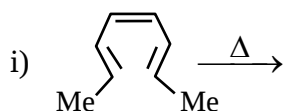
- iii) Explain the formation of a diacetal when D-glucose is treated with acetone under acidic condition, show how the reaction can be used for selective methylation of C₃-hydroxyl group of D-glucose.
- f) i) Write the products formed when ephedrine is subjected to Hofmann exhaustive methylation. [1½]
 ii) What happens when ephedrine is heated with conc. HCl? Explain the formation of the products. [1½]

Group – C

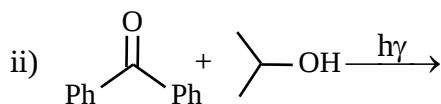
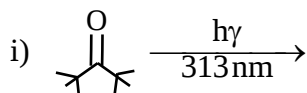
Unit - I

(Answer any one question)

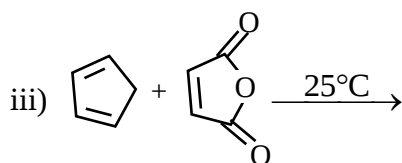
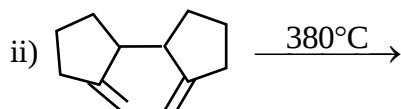
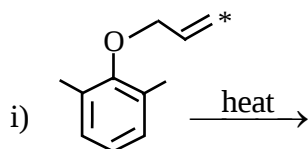
5. a) Give the product with its stereochemistry in the reactions given below : [2×3]



- b) Complete the following reactions and give their mechanisms : [2×2]

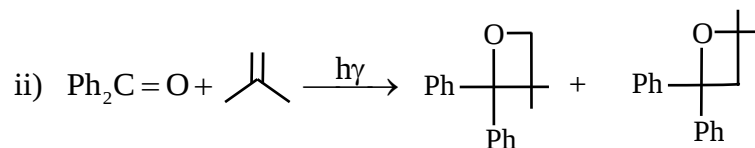
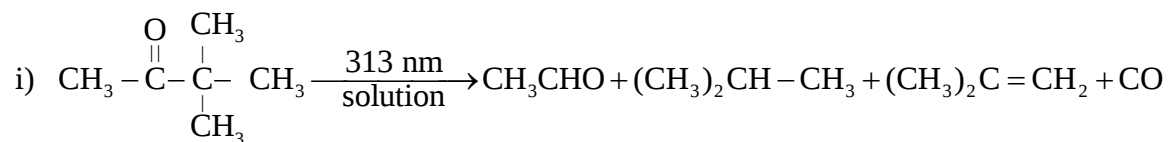


6. a) Complete the following reactions and give their mechanisms : [2×3]



b) Give mechanism for the formation of following products.

[2×2]



Unit - II

(Answer any one question)

7. a) Outline the synthesis of the tripeptide Ala.gly phe from L-amino acids. [3½]
 b) Convert : Acetamido malonic ester to tryptophan. [2]
 c) Write the structure of abietic acid and calculate the λ_{max} value using woodward's dime rules. [1½]
 d) Describe Edman method for sequential analysis of peptides. [3]
8. a) Discuss the role of DNFB for the determination of N-terminal residue of a peptide. [2]
 b) Convert glycine to phenylalanine by azlactone method. [3]
 c) Outline the synthesis of citral from acetone and ethyne. [3]
 d) Show how DCC is used for the activation of $-\text{CO}_2\text{H}$ group in peptide synthesis. [2]

